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Research Article

Catalytic Properties of Alumina-Supported Ruthenium, Platinum, and Cobalt Nanoparticles towards the Oxidation of Cyclohexane to Cyclohexanol and Cyclohexanone

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Abstract

A series of metal-loaded (Ru, Pt, Co) alumina catalysts were evaluated for the catalytic oxidation of cyclohexane using tertbutylhydroperoxide (TBHP) as oxidant and acetonitrile or acetic acid as solvent. These materials were prepared by the impregnation method and then characterized by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), H_2 chemisorption, Fourier Transformed Infrared Spectroscopy (FTIR), High-Resolution Transmission Electron Microscopy (HRTEM), and X-ray Diffraction (XRD). All the prepared materials acted as efficient catalysts. Among them, Ru/Al_2O_3 was found to have the best catalytic activity with enhanced cyclohexane conversion of 36 %, selectivity to cyclohexanol and cyclohexanone of 96 % (57.6 mmol), and cyclohexane turnover frequency (TOF) of 288 h^{-1}.

Keywords: Cyclohexane oxidation; Alumina-supported; ruthenium; platinum; cobalt; TBHP

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1. Introduction

The oxidation of organic substrates represents one of the most important industrial chemical reactions [1]. This explains the significant effort invested in research and development of new heterogeneous catalysts with increased activities and selectivities in these types of reactions. In particular, cyclohexane oxidation is one of the main goals in this area. The oxidation of cyclohexane to cyclohexanol and cyclohexanone is a key reaction in the synthesis of adipic acid (AA), which is an extremely important commodity chemical [2,3] mainly used in the production of urethanes and nylon-6, 6 (for fibers and resins). The global AA capacity, produced in 2006, was around 2.8 million metric tons and the demand for it has been growing, year after year, in the last decade [4]. The contemporary industrial process for manufacturing adipic acids (AA) is a two-step process involving nitric acid oxidation of KA oils, a mixture of cyclohexanol and cyclohexanone (which is produced from cyclohexane) using a homogeneous cobalt-based catalyst [5,6]. The main disadvantage of this process is that large amounts

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of nitrous oxide (N_2O) are released causing global warming and ozone depletion as well as acid rain and smog. Therefore, it is highly desirable to develop an alternate and effective green synthetic route for AA that is environmentally friendly [7-9].

Over the last decade, the research and development of transition metal nanoparticles have received a great deal of attention in many areas of science due to the fact that nanosized particles show different physical and chemical properties compared to those of the same materials in the bulk [10-13]. In recent years, many catalysts have been used for cyclohexane oxidation. For example, the catalytic oxidation of cyclohexane by O_2 over Au-Pd/MgO was reported by Liu *et al.* [14], in which conversion of 11 % and selectivity of 90.7 % were obtained, at 413 K and 3 bar O_2.

A series of cobalt-doped vanadium phosphorus oxides (VPO-Co) was synthesized by Mahdavi *et al.* [15] and used as catalysts in liquid oxidation of cyclohexane, with tertbutylhydroperoxide (TBHP) as oxidant; the conversion obtained was 65 % and the selectivity of cyclohexanol and cyclohexanone was 53 %, with reaction time of 8 h. Makgwane *et al.* [16] developed a hetero-mixed tungsten–vanadia (WO_3/V_2O_5) catalyst for cyclohexane oxidation, by using H_2O_2. Conversions up to 90 % were reached, while the total selectivity toward cyclohexanol and cyclohexanone was found around 65 %. In another study, Bellifa *et al.* [17] reported that vanadium-*titanium and* chromium– titanium *mixed oxides* MTiX (M = Cr and V) can catalyze the oxidation of cyclohexane using TBHP. The best result was obtained by V-TiO_2, with conversion of 35 % and olone selectivity of 92 %.

Hayati *et al.* [18] have used titanium modified octahedral manganese oxide Ti-OMS-2 in the oxidation of cyclohexane. They suggest that both titanium sites in frame-work and non-framework and the Lewis acidity created by the impregnation of Ti, increased the activity of OMS-2 in oxidation reactions. The conversion and selectivity of cyclohexanol and cyclohexanone are in the range of 4.4-7.8 and 89-92 %, respectively. On the other hand, Carabineiro *et al.* [19] tested gold nanoparticles supported on carbon materials for the oxidation of cyclohexane to cyclohexanol and cyclohexanone, under mild conditions (room temperature and atmospheric pressure), using an environmentally friendly oxidant (H_2O_2). The conversion was 3.6 % and the selectivity of cyclohexanol and cyclohexanone was 98 %.

Huang *et al.* [20] conducted a series of studies on cyclohexane by air oxidation; using boehmite ((AlOOH) immobilized cobalt tetra (4 carboxyl) phenylporphyrin catalyst (CoTCPP). Cyclohexane conversion of 19.6 % and selectivity of 73 % were obtained. Lu *et al.* [21] reported a 9.2 % conversion and 92.7 % selectivity when Co_3O_4 catalyst was used for the oxidation of cyclohexane with O_2, at 130 °C. Ti-Zr-Co alloys were prepared by Hao *et al.* [2], and then used as catalysts in solvent-*free liquid* phase oxidation of cyclohexane by oxygen; the conversion obtained was 6.8 % and the selectivity of cyclohexanol and cyclohexanone was 90.4 %.

In our present work, ruthenium, platinum and cobalt nanoparticles supported on alumina were used as catalysts for the aerobic oxidation of cyclohexane to KA oils (i.e., cyclohexanone and cyclohexanol), giving moderate yields and improved catalyst turnover number. Noble metals (Ru, Pt) are much active, stable and selective. They are widely used because of their better performance in many oxidation reactions. Cobalt was chosen due to it prevalent use in many oxidations, including that of cyclohexane commercially.

2. Materials and Methods

2.1 Catalyst preparation

2.1.1 Starting materials

The following chemicals were employed for the preparation of catalysts and in catalytic testing, namely Al_2O_3 (Oxid C Degussa), $Co(NO_3)_2.6H_2O$ (Fluka), $Pt(NH_3)_2(NO_2)_2$ (Alfa Aesar), $Ru(acac)_3$ (Strem Chemicals), tertiobutyl hydroperoxide (TBHP, Aldrich, 70 % in water), Cyclohexane (Prolabo), Acetonitrile (Aldrich), Acetic Acid (Aldrich), Triphenylephosphine (Aldrich).

2.1.2 Synthesis

The Al_2O_3 support of commercial grade was purchased in the form of nanopowder (in the range 10-50 nm). It required further treatment before impregnation of the metal precursors. The support was mixed with water (200 mL of H_2O for 100 g of support) in order to form a paste, which was dried overnight at 120 °C, and then sieved to retain only the particles having a diameter ranging between 0.1 and 0.25 mm. Then the support underwent calcination at 400 °C under oxidative flow (20 % O_2, 80 % Ar, 60 mL/min), during 4 h. After activation, Al_2O_3 showed a BET specific surface area of 95 m^2g^{-1}, pore volume of 0.72 cm^3g^{-1} and pore size of 31 nm.

An aqueous solution of $Pt(NH_3)_2(NO_2)_2$ and $Co(NO_3)_2.6H_2O$ or an acetone solution of $Ru(acac)_3$ was used for the wetness impregnation of the support, in order to obtain 1 or 5% wt. of metal catalyst. After solvent evaporation, the solids were dried at 120 °C overnight, then calcined at 400 °C (Co and Pt) and 350 °C (Ru), for 4 h, under oxidative atmosphere (Ar: 48 mL/min - O_2: 12 mL/min). Finally, the solids were reduced by H_2 (60 mL/min) at the same temperatures, for 4 h. These calcination and reduction temperatures for the ruthenium catalyst were selected because $Ru(acac)_3$ decomposes in air in one step, starting at 200 °C and completing at 350 °C. Activation at temperature as high as 350 °C ensures complete removal of acetylacetonate ligands from the ruthenium precursor [22].

2.2 Characterization of catalysts

The chemical compositions of the samples were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), using an OPTIMA 2000 DV spectrometer. Diffractograms of the catalysts were obtained from XRD experiments, performed on a Siemens D5005 powder diffractometer using Cu-Kα radiation (λ = 0.15186 nm) and a back monochromator. XRD patterns were recorded using a dwell time of 2 s, a step size of 0.04° and a constant divergence slit equal to 1°. The crystalline planes were identified by comparison with PDF standards from ICDD. The N_2 adsorption–desorption measurements of Al_2O_3 were carried out at -196 °C, using a Micromeritics TriStar device. The surface area of the support was calculated using the Brunauer-Emmett-Teller method.

Electron microscopy studies of the catalysts were carried out on a JEOL 2000 FX instrument, operating at 200 kV. Catalyst specimens for electron microscopy were prepared by grinding the powder samples in an agate mortar, suspending and sonicating them in ethanol, and placing a drop of the suspension on a holey carbon copper grid. After evaporation of the solvent, the specimens were introduced into the microscope column. The diameter distribution of the particles was determined by counting a large number of particles (>500) on the TEM micrographs and plotting n_i as a function of d_i (n_i is the number of particles within different intervals with given average diameters d_i). The mean surface diameter [23] of the particles is then given by Equation (1).

$$d = \sum n_i d_i^3 / \sum n_i d_i^2 \quad (1)$$

The measurements were done manually using the ImageJ program. The chemisorption measurements were carried out in a glass volumetric system. Catalyst samples of ~ 0.2 g were placed into a reactor and reduced by pure H_2, at 400 °C, for 2 h. A 1/1 H/metal stoichiometry was assumed, in order to calculate the metallic dispersion from which the mean diameter (d) of metal particles could be calculated using a cubic model, with one face in direct contact with the support (Equation (2)).

$$d(nm) = \frac{5x10^5}{\rho_M * S_M * D} \quad (2)$$

where ρ_M is the metal density, S_M surface area occupied per metal atom, and D the dispersion of the metal (Table 1) [24].

2.3 Evaluation of the catalytic activity

The catalytic oxidation of cyclohexane, with tertiobutylhydroperoxide (TBHP) as oxidant, was carried out in a glass round-bottom flask with a magnetic stirrer and a reflux condenser. First, commercial TBHP 70 % in H_2O (Aldrich) was stirred with cyclohexane in order to perform a phase transfer from water to cyclohexane. In a typical reaction, 60 mmol (6.5 mL) of cyclohexane and 60 mmol (8.5 mL) of oxidant (TBHP) are mixed in a closed Erlenmeyer flask and magnetically stirred for 24 h. The organic phase was then separated from the aqueous phase. In order to control the phase transfer, the concentration of the remaining TBHP, in the aqueous phase, was determined by iodometric titration, and was found to be < 10 %. The solvent (50 mL) was then added to the TBHP-cyclohexane mixture. These reactants

Table 1. Physico-chemical properties of metals

Metal	Molar mass ($g.mol^{-1}$)	Metal density ($g.cm^{-3}$)	Surface of atom (Å^2)	D × d (nm)
Ru	101.07	12.30	6.35	107.4
Pt	195.08	21.45	8.08	93.6
Co	58.93	8.90	5.43	101.22

and the solvent were introduced in a glass round-bottom flask and heated to 70 °C under vigorous stirring. The catalyst (0.05 g) was subsequently added to the reaction mixture (time zero). The reaction products were identified by comparison with authentic products and the course of reactions was followed by gas chromatography (GC), using a Varian CP-3800 gas chromatograph equipped with a CP-WAX 52 CB column. A flame ionization detector (FID) was used and a quantity of 0.5 µL from the sample was analyzed. Before GC analysis, the remaining TBHP was decomposed by introducing an excess of triphenylphosphine. On the other hand, to control this remaining TBHP, an iodometric titration was performed at the end of the reaction (after 6 h) by testing the organic phase. The catalytic performances were reported in terms of cyclohexane conversion and selectivity towards products. They are calculated following the expressions in Equations (3-4):

$$Conversion\,(\%) = 100\,x\,\frac{[C_6H_{12}]_0 - [C_6H_{12}]_e}{[C_6H_{12}]_0} \qquad (3)$$

$$Selectivity\,(\%) = 100\,x\,\frac{moles\,of\,individual\,product}{moles\,of\,total\,product} \qquad (4)$$

3. Results and Discussion

3.1 Characterization

As measured by ICP-OES, the metal content in all catalysts is either 1 or 5 % (Table 2). Figure 1 shows the XRD patterns of the bare Al_2O_3 support and the different catalysts. The alumina support shows two crystalline phases with sharper peaks, indicating that alumina is in δ and γ forms. The diffractogram of Ru/Al_2O_3 confirms that metallic ruthenium is present in catalysts as a result of the reduction operation, and no RuO_2 peak is observed. The Ru diffraction peaks (38.4°, 42.2°, 44.0°, 58.3°, and 69.4° 2θ, JCPDS no. 6-663) are sufficient for an estimation of the average ruthenium crystallite size, which is 9 nm, with a relative standard deviation of 10 %. Diffraction peaks at 39.76°, 46.24° and 67.45° 2θ (JCPDS no. 4-802), characteristic of metallic Pt, were detected on the diffraction patterns of Pt/Al_2O_3. No platinum oxide was observed. Crystalline Co_3O_4 and CoO phases were observed in Co/Al_2O_3. No peaks of metallic Co were detected. The peaks at 19.08°, 31.38°, 36.88°, 44.88°, 59.38° and 65.28° 2θ were attributed to the cubic phase of Co_3O_4 with Fd3m space group (JCPDS no. 42-1467). In addition, the lines at 42.4° and 34.5° 2θ could be assigned to the cubic structures of CoO (JCPDS no. 71-1178).

The metal dispersion of catalysts was obtained by H_2 chemisorption. The percentage of metallic dispersion was calculated, assuming an H/M atomic ratio equal to 1 [25,26], as shown in Table 2. The 1 % Ru or Pt catalysts gave a dispersion (20 %) lower than that obtained with the 5 % catalysts. Ruthenium catalysts showed higher dispersion than platinum ones. DRX results of cobalt catalysts showed the formation of cobalt oxides and chemisorption measurements were not possible.

TEM analysis (micrographs and histograms) for Ru/Al_2O_3, Pt/Al_2O_3 and Co/Al_2O_3

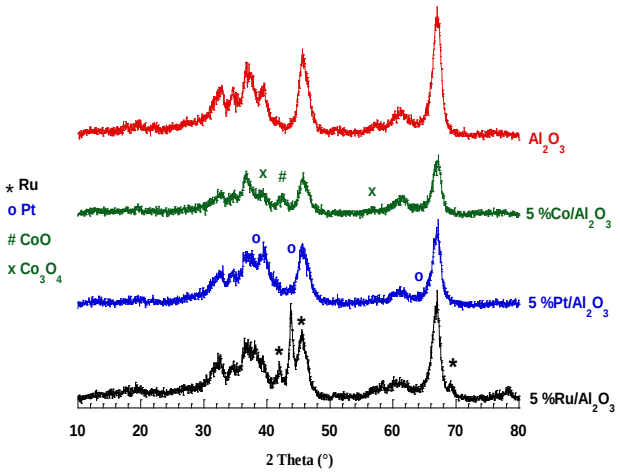

Figure 1. X-ray diffraction (XRD) patterns of catalysts

Table 2. Metallic accessibility and crystallite size for various catalysts

Catalyst	ICP (wt.%)	Chemisorption		TEM	
		Dispersion (%)	Particle size[a] (nm)	Dispersion (%)	Particle size[b] (nm)
Ru/Al_2O_3	1.02	20	5.3	18	5.8
	5.09	45	2.4	42	2.5
Pt/Al_2O_3	1.02	20	4.7	23	4.0
	5.06	28	3.3	29	3.2
Co/Al_2O_3	1.07	/	/	/	/
	5.08	/	/	/	/

systems are shown in Figures 2, 3, and 4, respectively. The 5 %Pt/Al_2O_3 and 5 %Ru/Al_2O_3 catalyst samples were well dispersed with no indication of agglomeration of the metal particles. All of these materials have a spherical morphology. The ruthenium system showed nanoparticle sizes ranging from 1.7 to 4.6 nm with a mean size of 2.5 nm (Figure 2).

In the platinum system, the size distribution ranges between 1.8 and 6 nm, with a mean particle size of 3.2 nm (Figure 3). TEM analysis of Co/Al_2O_3 (Figure 4) revealed an intensive agglomeration of cobalt particles on these samples and, then, a true reliable distribution could not be given. The average size of these agglomerations was between 8 and 10 nm. Zhou *et al.* [5] showed that Co_3O_4 oxide has a platelet morphology forming, in most cases, quite large agglomerations. As shown, a very good correspondence between the mean particle sizes estimated from H_2 chemisorption and TEM was obtained for all catalyst samples (Ru and Pt) (Table 2).

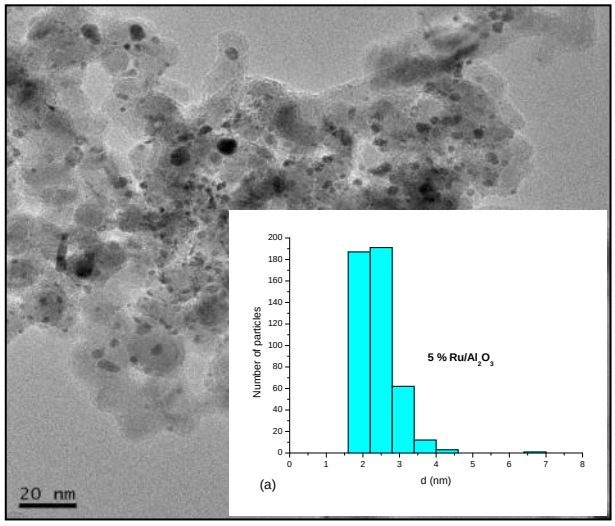

Figure 2. Micrography and histogram for 5 %Ru/Al_2O_3

3.2 Catalytic oxidation of cyclohexane

The activities of the catalysts for the catalytic oxidation of cyclohexane with TBHP at 70 °C, in acetic acid or acetonitrile, are presented in Table 3. The desired products are cyclohexanol ($C_6H_{11}OH$) and cyclohexanone ($C_6H_{10}O$), but other products like cyclohexyl hydroperoxide, adipic acid, ester dicyclohexyl adipate, hexanolactone, and other esters [5], among which is cyclohexyl acetate [27], did also form. In general, cyclohexyl hydroperoxide can be decomposed to cyclohexanol and cyclohexanone in presence of PPh_3 (triphenylphosphine) introduced before GC analysis, thus increasing the yield of the target compounds.

The present study focused on the selectivity towards olone only (cyclohexanol and cyclohexanone). The amount of catalyst used was 0.05 g and the cyclohexane to TBHP mole ratio was (1:1). A blank oxidation reaction (i.e. without catalyst) was carried out under typical reaction conditions and no oxidation product was formed. Moreover, to check the impact of the support on the cyclohexane oxidation reaction, Al_2O_3 was tested for its catalytic properties in the presence of acetic acid as solvent. The support exhibited a conversion less than 15 % with selectivity around 10.3 mmol (17.2 %) (Olone). As expected, these results are found to be close to those of Bellifa *et al.* [28] and Zhao *et al.*

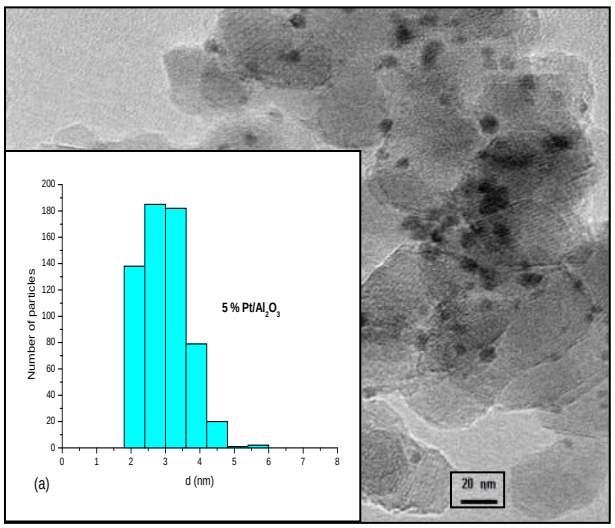

Figure 3. Micrography and histogram of 5 % Pt/Al_2O_3

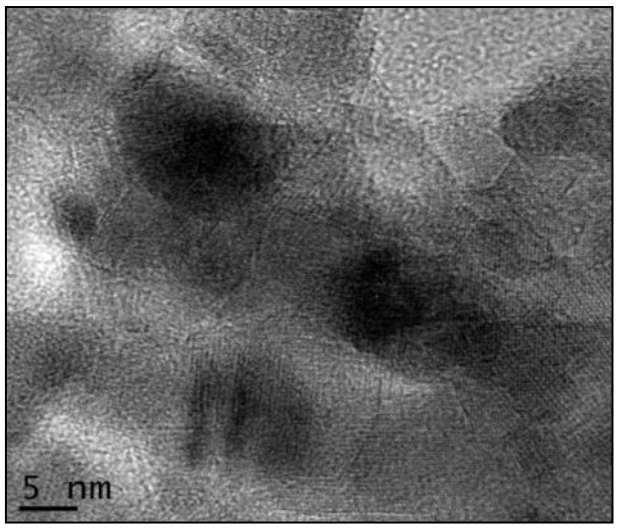

Figure 4. Micrography of 5 % Co/Al_2O_3

[29]. Table 3 details the catalytic activities of alumina-supported ruthenium in the presence of acetic acid and acetonitrile. Cyclohexanol and cyclohexanone selectivities increase with metal content [17]. The 1 % catalysts showed a modest selectivity increase compared to 5 % ones. So, one can assume that the support participates in the reaction via a functional mechanism (support and metal), as reported by Wangcheng *et al.* [30].

In the presence of TBHP and acetic acid as solvent, turnover frequencies (TOF) of 1863 h^{-1} and 288 h^{-1} were obtained, after 6 h of catalytic oxidation, for 1 % and 5 % Ru/Al_2O_3 systems, respectively. The TOF values obtained are comparable (1907 h^{-1} for 1.21 % Au/MCM-41) [31] to or higher (184 h^{-1}) [32] than those of $CoFe_2O_4$ catalysts reported in the literature; however they are smaller than the highest value which amounts to 11900 h^{-1} for Au/ HAP (Hydroxyapatite) [33], and 2592 h^{-1} for 1 % Au/Al_2O_3. Nevertheless, gold-based catalysts are regarded as expensive catalysts compared to ruthenium based catalyst which is the least expensive among the noble metals. This represents a cyclohexane conversion of 35.6 %, whereas the selectivity towards the formation of cyclohexanol is 10.0 mmol (16.7 %) and towards cyclohexanone 12.4 mmol (20.7 %). By comparing the two solvents, the activities obtained under acidic conditions were found to be higher compared to those obtained in acetonitrile. These activities decreased when the ruthenium content increased. This observation suggests that the acetic acid was oxidized by TBHP to form peracetic acid in situ, which served as a better oxidant [34,36]. The amount of ruthenium leached, of our nanostructured material, is determined after reaction and found < 50 ppm.

Platinum catalysts (Table 3), in acetic acid and after 6 h, showed high activity towards cyclohexane oxidation, and gave turnovers of 2830 h^{-1} and 782 h^{-1}, for 1 % and 5 % Pt/Al_2O_3, respectively. These correspond to conversions 14.8 % and 28.4 %, respectively. In the presence of acetonitrile, it is clear that platinum does not promote the formation of cyclohexanone. The cyclohexanol selectivity decreases when the platinum content increases from 1 to 5 % [30]. As can be seen from the comparison data, the ruthenium-based catalyst is more active towards oxidation products than the platinum-based catalyst.

After the reaction, the ICP analysis of platinum-based catalyst did not exhibit leaching, which means that it is a heterogeneous catalytic system. For cobalt nanoparticles supported on alumina, the results reveal that these solids are capable of oxidizing the substrate used in this study. After 6 h of reaction time, and in the presence of acetic acid as solvent, the turnovers were found equal to 177 h^{-1} and 49 h^{-1} , which correspond to 14.8 % and 20.7 % conversions to cyclohexane, for 1 % and 5 % Co_xO_y /Al_2O_3, respectively (Table 3). These results show that cobalt-based catalysts are less active than their ruthenium and platinum counterparts, in the conditions under consideration. It can be seen from Table 3 that a relatively lower conversion was obtained in the case of acetonitrile. The chemical analysis of the catalyst, after reaction, revealed that 20 % of cobalt, which was in the catalyst, passed into the solution. Therefore, it is not possible to check whether the catalysis took place in the heterogeneous system Co_xO_y/Al_2O_3, in a mixture of heterogeneous and homogeneous catalysts, or just as a homogeneous system.

Table 3. Oxidation of cyclohexane with M/Al_2O_3 catalysts

Catalyst	wt. (%)	Acetic acid				Acetonitrile			
		Products (%)		TOF (h^{-1})	Conv[b] (%)	Products (%)		TOF (h^{-1})	Conv[b] (%)
		Alcohol	Ketone			Alcohol	Ketone		
Al_2O_3	/	12.2	5.0	2.9[a]	14	0.0	0.0	0	0
Ru/Al_2O_3	1.02	7.2	18.4	1863	18.8	34.2	26.3	624	6.3
	5.09	16.7	20.7	288	35.6	17.2	20.3	238	29.4
Pt/Al_2O_3	1.02	22.5	6.4	2830	14.8	35.0	0.0	1377	7.2
	5.06	16.7	4.2	782	28.4	5.0	0.0	481	17.5
Co/Al_2O_3	1.07	11.2	5.7	177.4[a]	14.8	7.0	4.2	145[a]	12.3
	5.08	23.4	6.7	48.8[a]	20.7	5.0	3.7	65.6[a]	27.8

C_6H_{12} = 6.5 mL; TBHP = 8.5 mL; solvent = 50 mL; catalyst = 0.05 g; t = 6 h; T = 70°C;
TOF = mole of converted cyclohexane per unit time per mole of dispersed ruthenium or platinum.
[a] TOF : mole of converted cyclohexane per unit time per mole of cobalt or Al_2O_3.
[b] After 6 h of reaction time

In summary, one can say that concerning the catalytic activity and selectivity of alumina-supported ruthenium, platinum and cobalt nanoparticle towards the oxidation reaction of cyclohexane, it can be proven that noble and non-noble metals can be active for the oxidation of cyclohexane. The support is active during the cyclohexane oxidation, but the presence of the metal clearly improves the reaction activity which increases with the metal loading. From the literature, it is well established that some transition metal ions can be catalytically activated towards the oxidation reactions of certain organic substrates when H_2O_2 or RO_2H are used as oxidizing agents.

These reactions can be classified in two categories, depending on whether the active species in the oxidation reaction is (i) peroxometal or (ii) oxometal [37]. Generally, the last transition metals employ an oxometal intermediate. Some other elements, such as vanadium, can use either route, depending on the substrate. Most transition metals that catalyze oxygen-transfer processes, whether via peroxometal or oxometal, are also able to catalyze processes via free radicals formed from peroxide compounds [38,40].

Thus, as expected in the cyclohexane oxidation reaction, and in the presence of the two solvents, the activity increases as $Ru/Al_2O_3 > Pt/Al_2O_3 > Co/Al_2O_3$. The acetic acid when used as solvent is better than acetonitrile, as it allows higher conversion and selectivity towards cyclohexanol and cyclohexanone. From the leaching results, it is possible to state that the systems studied have the following order of stability: $Pt/Al_2O_3 > Ru/Al_2O_3 > Co_xO_y /Al_2O_3$.

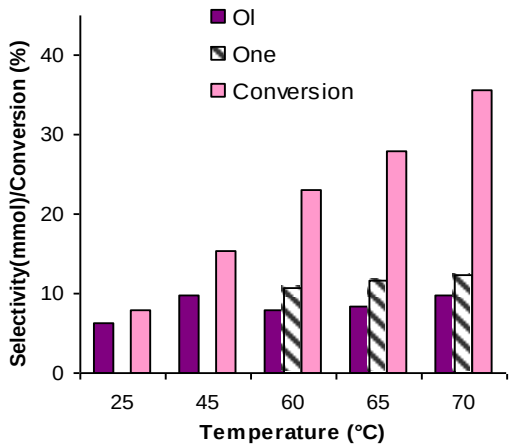

Figure 5. Effects of reaction temperature on conversion and selectivity over 5 %Ru/Al_2O_3; C_6H_{12} = 6.5 mL, TBHP = 8.5 mL, acetic acid = 50 mL, catalyst = 0.05 g, t = 6 h

3.2.1 Optimization of reaction conditions

Due to the good performance of the catalyst Ru/Al_2O_3, this study focused, in the following section, on the influence of various parameters on cyclohexane conversion and selectivity towards cyclohexanone and cyclohexanol over 5 % Ru/Al_2O_3. The reaction conditions were optimized in acetic acid. The reactions were conducted at the temperatures 25, 45, 60, 65, and 70 °C, as shown in Figure 5.

As expected, the cyclohexane conversion increases as a function of the temperature. The distribution of cyclohexanol and cyclohexanone shows no formation of cyclohexanone at 25 and 45 °C, and a temperature increase clearly favors the production of cyclohexanone. A similar behavior was noted by Zhou *et al.* [5], and Yuan *et al.* [41]. These results show that when the temperature increased from 25 to 70 °C, the conversion and selectivity towards cyclohexanone and cyclohexanol increased and

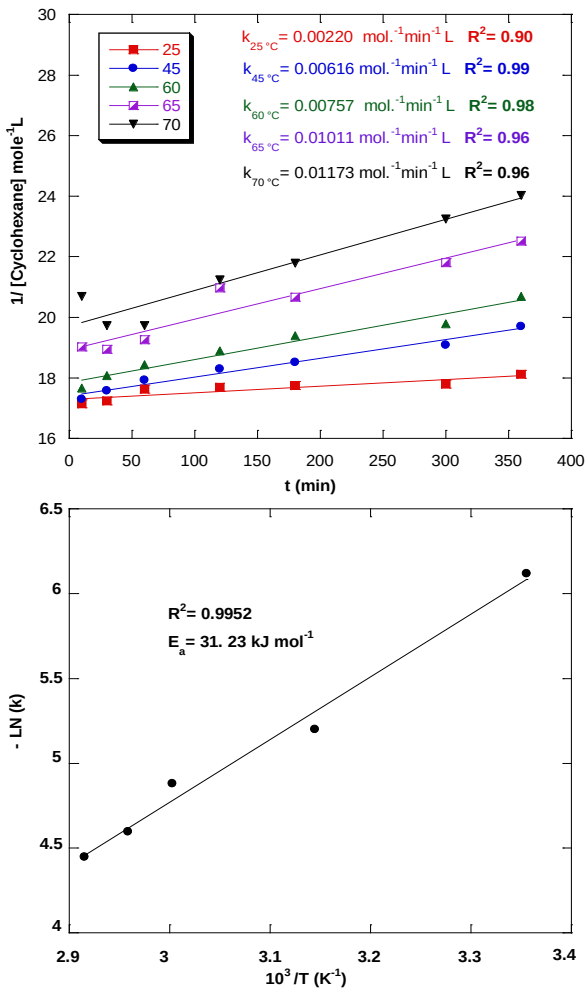

Figure 6. Kinetic data at different temperatures and Arrhenius plot for the oxidation of cyclohexane

reached their maxima. To test the order of the reaction, both $ln\ [A]/[A]_o$ and $1/[A]$ were plotted against t for the reactions.

The second order plots gave a straight line, indicating that the reaction is of the 2nd order, as shown in Figure 6. The activation energy, calculated from the slope of the straight line (Figure 6), is 31.23 kJ mol^{-1}, which is lower than the values reported in several previous works [42-47]. The effect of the mole ratio was examined by varying the cyclohexane/TBHP mole ratios (1:1 and 1:2), with 0.05 g of Ru/Al_2O_3 catalyst at 70 °C, for 6 h (Figure 7). An increase in the TBHP concentration (1:2) resulted in an increase in the selectivity of the oxidized products, such as: cyclohexanol (from ~10 mmol (16.7 %) to 20 mmol (33.4 %)) and cyclohexanone (from 12.4 mmol (20.7 %) to 37 mmol (61.7 %)); however, the conversion remained constant (35.6 %). This might be explained by the fact that the TBHP used may have increased the conversion of cyclohexanol, which in turn reacted with the acetic acid in excess, which led to an increase in cyclohexanone formation.

A similar behavior was noted on TS-1 [48]. On the other hand, TBHP gave cyclohexanone as the major product, owing to its much stronger oxidizing capability. The same observation was reported by Selvam *et al.* [49] and Kumar *et al.* [27]. According to them, the increase in the cyclohexanone selectivity, with the increase in TBHP, is due to the oxidation of cyclohexanol to cyclohexanone in the presence of excess amount of TBHP.

The effects of the amount of catalyst on the reaction were also studied. The results are presented in Figure 8. One can see that the olone selectivity increased from 22 mmol (~ 37 %) to 57.6 mmol (96 %), while the conversion decreased from 35.6 % to 25 %, as the mass of catalyst rose from 0.05 g to 0.1 g. These results coincide with those of Lu *et al.* [21]. The presence of a high number of active centers eventually causes an increase in the rate of reaction, thereby increasing the olone selectivity. On the other hand, these results indicate that in the system catalyzed by Ru/Al_2O_3, only a small amount of catalyst was active in the oxidation of cyclohexane [22]. This could also be attributed to the competition of interactions between the metal-oxo species in the catalyst and the hydroperoxy species and cyclohexane [50, 51]. It can therefore be concluded that the amount of 0.1 g of catalyst is optimal for this catalytic system.

The effect of ruthenium loading on the oxidation of cyclohexane was also examined. The cyclohexane conversion, as well as the (cyclohexanone + cyclohexanol) selectivity over different Ru-loaded catalysts, is shown in Figure 9. However, as the ruthenium loadings of our samples increased from 0 to 5.0 %, the cyclohexane conversion and the total selectivity of the oxygenated products increased, while the TOF value decreased. This behavior is closely related to the size of Ru particles. The catalyst 5% Ru/Al_2O_3 exhibited the smallest and most uniform Ru particles (with an average size of about 2.5 nm), followed by catalysts 3.7 % Ru/Al_2O_3 (about 4.4 nm in size) and 1 %

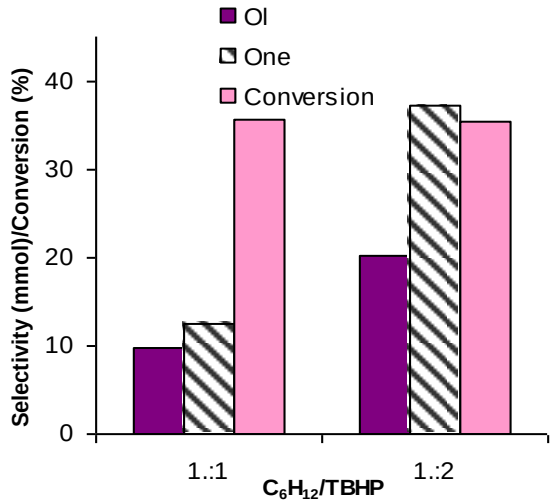

Figure 7. Effects of C_6H_{12}/TBHP mole ratio on conversion and selectivity over 5%Ru/Al_2O_3; Acetic acid = 50 mL; catalyst = 0.05 g; t = 6 h; T = 70 °C

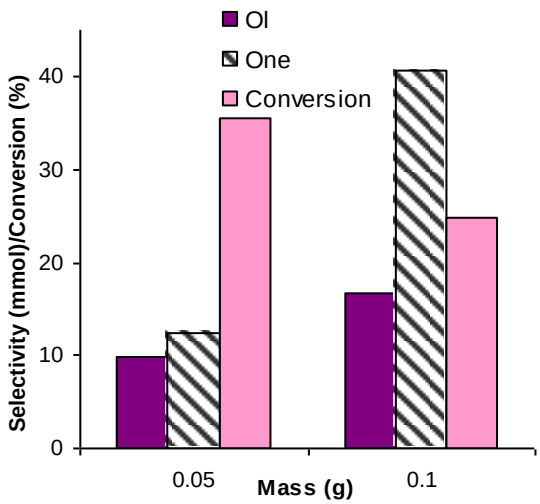

Figure 8. Effects of the amount of catalyst on conversion and selectivity over 5 %Ru/Al_2O_3; C_6H_{12} = 6.5 mL; TBHP = 8.5 mL; Acetic acid = 50 mL; T = 70 °C; t = 6 h

Ru/Al_2O_3 (around 5.8 nm). The high activity of the catalyst, which contains small size Ru particles, may be explained as follows. This result was expected, because small particles have a higher density, which gives a more active surface of Ru atoms. This is favorable for the adsorption and activation of the oxidant during the oxidation reaction, resulting in a higher catalytic activity [50,52]. It is therefore clear that the catalytic activity depends on the Ru particle size. Another reason for the low catalytic activity, with low ruthenium concentrations, may be due to partial incorporation of Ru into the bulk support [53].

In addition, in order to check the catalyst recyclability, five reaction runs were carried out under typical reaction conditions, using acetic acid as solvent. The results are shown in Figure 10. After each reaction, the catalyst was separated by filtration, and then reused under the same reaction conditions. After deactivation, it was dried at 350 °C, for 2 h, under argon. The regenerated catalyst was examined under the same conditions.

It can be seen that the olone selectivity decreases with the number of reaction runs, and after the fifth run the catalyst is completely deactivated. The selectivity towards cyclohexanol and cyclohexanone on a recycled catalyst was slightly lower than that obtained on a fresh one. The deactivation of the catalyst is likely related to common inhibition processes found in oxidation reactions, such as the adsorption of the oxygenated product species on the catalyst surfaces [54]. These results disclose the fact that the catalyst is stable or could be recycled after the reaction.

4. Conclusions

Various metal-supported alumina catalysts were prepared by the incipient wetness impregnation method. The characterization of the catalysts obtained, confirmed that ruthenium and platinum are in metallic form while cobalt is in the form of oxides Co_3O_4 and CoO. The liquid-phase oxidation of cyclohexane was performed using tertbutyl hydroperoxide (TBHP) at 70 °C. The support Al_2O_3 was active during the oxidation of cyclohexane but the presence of a metal clearly improved the activity of the reaction. All the prepared catalysts showed higher catalytic activity and stability for the oxidation of cyclohexane in acetic acid, compared to acetonitrile. All the prepared catalysts exhibited high catalytic activities and could reach a cyclohexane conversion of 35.6 % and selectivity of 57.6 mmol towards the desired products (olone).

Several reaction parameters in the cyclohexane oxidation reaction over 5 $\%Ru/Al_2O_3$, i.e. the temperature, amount of catalyst and concentration of TBHP in terms of the cyclohexane/TBHP ratio, were optimized to achieve maximum selectivity to cyclohexanol and cyclohexanone. After optimization of these parameters, the best reaction conditions were obtained for 0.1 g of catalyst, T = 70 °C, C_6H_{12}/TBHP molar ratio =1:2 and t = 6 h. The catalyst was recycled and reused five times. It exhibited practically the same activity and selectivity as those of fresh catalyst after heat treatment, under argon.

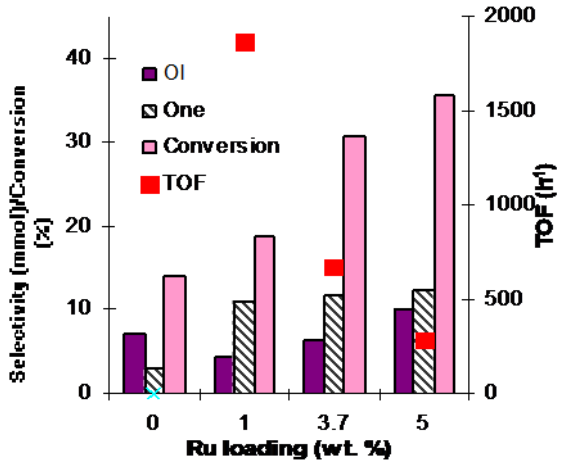

Figure 9. Effect of Ru loading on conversion and selectivity over x $\%Ru/Al_2O_3$; Acetic acid = 50 mL; Catalyst = 0.05 g; t = 6 h; T = 70 °C

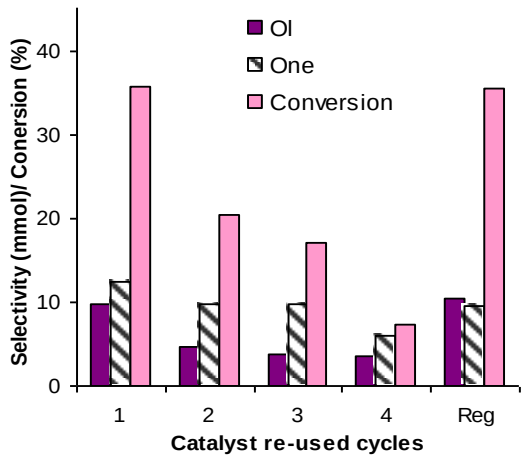

Figure 10. Catalyst recycling for cyclohexane oxidation over 5 $\%Ru/Al_2O_3$; C_6H_{12} = 6.5 mL; TBHP = 8.5 mL; acetic acid = 50 mL; catalyst = 0.05 g; t = 6 h; T = 70 °C

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References

[1] Sheldon, R.A. (1981) Metal-catalyzed Epoxidation of Olefins with Hydroperoxides, in *Aspects of Homogeneous Catalysis*, R. Ugo (Ed.); Reidel, Dordrecht, Volume 4, pp. 3-70.

[2] Hao, J., Liu, B., Cheng, H., Wang, Wang, Q.J., Cai, S., Zhao, F. (2009). Cyclohexane Oxidation on A Novel $Ti_{70}Zr_{10}Co_{20}$ Catalyst Containing Quasicrystal. *Chemical Communications*, 23: 3460-3462.

[3] Sato, K., Aoki, M., Noyori, R. (1998). A "Green" Route to Adipic Acid: Direct Oxidation of Cyclohexenes with 30 Percent Hydrogen Peroxide. *Science*, 281: 1646-1647.

[4] Cavani, F., Centi, G., Perathoner, S., Trifiro, F. (2009). *Sustainable Industrial Processes*, WILEY-VCH Verlag GmbH & Co, KGaA, Weinheim.

[5] Zhou, L., Xu, J., Miao, H., Wang, F., Li, X. (2005). Catalytic Oxidation of Cyclohexane to Cyclohexanol and Cyclohexanone over Co_3O_4 Nanocrystals with Molecular Oxygen. *Applied Catalysis A: General,* 292: 223-228.

[6] Chen, C., Xu, J., Zhang, Q., Ma, H., Miao, H., Zhou, L. (2009). Direct Synthesis of Bifunctionalized Hexagonal Mesoporous Silicas and Its Catalytic Performance for Aerobic Oxidation of Cyclohexane. *The Journal of Physical Chemistry C*, 113: 2855-2860.

[7] Deng, Y., Ma, Z., Wang, K., Chen, J. (1999). Clean Synthesis of Adipic Acid by Direct Oxidation of Cyclohexene with H_2O_2 over Peroxytungstate-Organic Complex Catalysts. *Green Chemistry*, 1: 275-276.

[8] Thomas, J.M., Raja, R. (2006). Innovations in Oxidation Catalysis Leading to A Sustainable Society. *Catalysis Today*, 117: 22-31.

[9] Guo, C.C., Chu, M.F., Liu, Q., Liu, Y., Guo, D.C., Liu, X.Q. (2003). Effective Catalysis of Simple Metalloporphyrins for Cyclohexane Oxidation with Air in the Absence of Additives and Solvents. *Applied Catalysis A: General*, 246: 303-309.

[10] Burda, C., Chen, X., Narayanan, R., El-Sayed, M.A. (2005). Chemistry and Properties of Nanocrystals of Different Shapes. *Chemical Reviews*, 105: 1025-1102.

[11] Wang, C., Chen, L., Qi, Z. (2013). One-pot Synthesis of Gold Nanoparticles Embedded in Silica for Cyclohexane Oxidation. *Catalysis Science & Technology*, 3: 1123-1128.

[12] Wu, P., Xiong, Z., Loh, K.P., Zhao, X.S. (2011). Selective Oxidation of Cyclohexane over Gold Nanoparticles Supported on Mesoporous Silica Prepared in the Presence of Thioether Functionality. *Catalysis Science & Technology*, 1: 285-294.

[13] Bradley, J.S. In: Schmidt G., editor. (1994). *Clusters and Colloids from Theory to Applications*, VCH, Weinheim, Germany.

[14] Liu, X., Conte, M., Sankar, M., He, Q., Murphy, D.M., Morgan, D., Jenkins, R.L., Knight, D., Whiston, K., Kiely, C.J., Hutchings, G.J. (2015). Liquid Phase Oxidation of Cyclohexane Using Bimetallic Au-Pd/MgO Catalysts. *Applied Catalysis A: General*, 504: 373-380.

[15] Mahdavi, V., Hasheminasab, H.R. (2015). Liquid-phase Efficient Oxidation of Cyclohexane over Cobalt Promoted VPO Catalyst Using Tert-butylhydroperoxide. *Journal of the Taiwan Institute of Chemical Engineers*, 51: 53-62.

[16] Makgwane, P.R., Ray, S.S. (2014). Efficient Room Temperature Oxidation of Cyclohexane over Highly Active Hetero-mixed WO_3/V_2O_5 Oxide Catalyst. *Catalysis Communications*, 54: 118-123.

[17] Bellifa, A., Choukchou-Braham, A., Kappenstein, C., Pirault-Roy, L. (2014). Preparation and Characterization of MTiX for the Catalytic Oxidation of Cyclohexane. *RSC Advances*, 4: 22374-22379.

[18] Hayati, F., Chandren, S., Hamdan, H., Nur, H. (2014). The Role of Ti and Lewis Acidity in Manganese Oxide Octahedral Molecular Sieves Impregnated with Titanium in Oxidation Reactions. *Bulletin of Chemical Reaction Engineering & Catalysis*, 9: 28-38.

[19] Carabineiro, S.A.C., Martins, L.M., Avalos-Borja, M., Buijnsters, J.G., Pombeiro, A.J.L., Figueiredo, J.L. (2013). Gold Nanoparticles Supported on Carbon Materials for Cyclohexane Oxidation with Hydrogen Peroxide. *Applied Catalysis A: General*, 467: 279-290.

[20] Huang, G., Shen, L., Luo, Z.C., Hu, Y.D., Guo, Y.A., Wei, S.J. (2013). Use of A Boehmite Immobilized Cobalt Tetra(4-carboxyl) Phenylporphyrin Catalyst for the Aerobic Oxidation of Cyclohexane to Ketone and Alcohol. *Catalysis Communications*, 32: 108-112.

[21] Lu, X.H., Yuan, H.X., Lei, J., Zhang, J.L., Yu, A.A., Zhou, D., Xia, Q.H. (2012). Selective Oxidation of Cyclohexane to KA-oil with Oxygen over Active Co_3O_4 in A Solvent-free System. *Indian Journal of Chemistry*, 51A: 420-427.

[22] Bernas, A., Kumar, N., Laukkanen, P., Vayrynen, J., Salmi, T., Murzin, D.Y. (2004). Influence of Ruthenium Precursor on Catalytic Activity of Ru/Al_2O_3 Catalyst in Selective Isomerization of Linoleic Acid to Cis-9,trans-11- and Trans-10,cis-12-conjugated Linoleic Acid. *Applied Catalysis A: General*, 267: 121-133.

[23] Perkas, N., Minh, D.P., Gallezot, P., Gedanken, A., Besson, M. (2005). Platinum and Ruthenium Catalysts on Mesoporous Titanium and Zirconium Oxides for the Catalytic Wet Air Oxidation of Model Compounds. *Applied Catalysis B: Environmental*, 59: 121-130.

[24] Bergeret, G., Gallezot, P. (1997). In: *Handbook of Heterogeneous Catalysis*. Wiley-VCH, Weinheim.

[25] Coloma, F., Sepulveda-Escribano, A., Fierro, J.L., Rodriguez- Reinoso, F. (1997). Gas Phase Hydrogenation of Crotonaldehyde over Pt/Activated Carbon Catalysts: Influence of the Oxygen Surface Groups on the Support. *Applied Catalysis A: General*, 150: 165-183.

[26] Rekkab-Hammoumraoui, I., Choukchou-Braham, A., Pirault-Roy, L., Kappenstein, C. (2011). Catalytic Oxidation of Cyclohexane to Cyclohexanone and Cyclohexanol by Tert-Butyl Hydroperoxide over Pt/oxide Catalysts. *Bulletin of Materials Science*, 34: 1127-1135.

[27] Kumar, R., Sithambaram, S., Suib, S.L. (2009). Cyclohexane Oxidation Catalyzed by Manganese Oxide Octahedral Molecular Sieves-Effect of Acidity of the Catalyst. *Journal of Catalysis,* 262: 304-313.

[28] Bellifa, A., Lahcene, D., Tchenar, Y.N., Choukchou-Braham, A., Bachir, R., Bedrane, S., Kappenstein, C. (2006). Preparation and Characterization of 20 wt.% V_2O_5-TiO_2 Catalyst Oxidation of Cyclohexane. *Applied Catalysis A: General*, 305: 1-6.

[29] Zhao, R., Wang, Y., Guo, Y., Guo, Y., Liu, X., Zhang, Z., Wang, Y., Zhan, W., Lu, G. (2006). A Novel Ce/AlPO-5 Catalyst for Solvent-free Liquid Phase Oxidation of Cyclohexane by Oxygen. *Green Chemistry*, 8: 459-466.

[30] Wangcheng, Z., Guanzhong, L., Yanglong, G., Yun, G., Yanqin, W., Yunsong, W., Zhigang, Z., Xiaohui, L. (2008). Synthesis of Cerium-doped MCM-48 Molecular Sieves and Its Catalytic Performance for Selective Oxidation of Cyclohexane. *Journal of Rare Earths,* 26: 515-522.

[31] Lu, G., Zhao, R., Qian, G., Qia, Y., Wang, X., Suo, J. (2004). A Highly Efficient Catalyst Au/MCM-41 for Selective Oxidation Cyclohexane Using Oxygen. *Catalysis Letters*, 97: 115-118.

[32] Li, H., She, Y., Wang, T. (2012). Advances and Perspectives in Catalysts for Liquid-phase Oxidation of Cyclohexane. *Frontiers of Chemical Science and Engineering*, 6: 356-368.

[33] Liu, Y., Tsunoyama, H., Akita, T., Xie, S., Tsukuda, T. (2011). Aerobic Oxidation of Cyclohexane Catalyzed by Size-Controlled Au Clusters on Hydroxyapatite: Size Effect in the Sub-2 nm Regime. *ACS Catalysis*, 1: 2-6.

[34] Rekkab-Hammoumraoui, I., Benabadji-Soulimane, R., El Korso-Hamza Reguig, S., Choukchou-Brabam, A., Bachir, R. (2010). Preparation and Characterization of X wt-%Ru/Al_2O_3 Catalysts for Cyclohexane Oxidation Using Tert-butyl Hydroperoxide. *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, 1: 240-239.

[35] Sooknoi, T., Limtrakul, J., (2002). Activity Enhancement by Acetic Acid in Cyclohexane Oxidation Using Ti-containing Zeolite Catalyst. *Applied Catalysis A: General*, 233: 227-237.

[36] Adam, F., Wong, J., Ng, E. (2013). Fast Catalytic Oxidation of Phenol over Iron Modified Zeolite L Nanocrystals. *Chemical Engineering Journal*, 214: 63-67.

[37] Arends, I.W.C.E., Sheldon, R.A. (2001). Activities and Stabilities of Heterogeneous Catalysts in Selective Liquid Phase Oxidations: Recent Developments. *Applied Catalysis A: General*, 212: 175-187.

[38] Fraile, J.M., Garcia, J.I., Mayoral, J.A., Vispe, E. (2001). Effect of the Reaction Conditions on the Epoxidation of Alkenes with Hydrogen Peroxide Catalyzed by Silica-Supported Titanium Derivatives. *Journal of Catalysis*, 204: 146-156.

[39] Busca, G., Finocchio, E., Ramis, G., Ricchiardi, G. (1996). On the Role of Acidity In Catalytic Oxidation. *Catalysis Today*, 32: 133-143.

[40] Conte, M., Liu, X., Murphy, D.M., Whiston, K., Hutchings, G.J. (2012). Cyclohexane Oxidation Using Au/MgO: An Investigation of the Reaction Mechanism. *Physical Chemistry Chemical Physics,* 14: 16279-16285.

[41] Yuan, H.X., Xia, Q.H., Zhan, H.J., Lu, X.H., Su, K.X. (2006). Catalytic Oxidation of Cyclohexane to Cyclohexanone and Cyclohexanol by Oxygen in A Solvent-free System over Metal-containing ZSM-5 Catalysts. *Applied Catalysis A: General*, 304: 178-184.

[42] Kharkova, T.V., Arest-Yakubovich, I.L., Lipes, V.V. (1989). Kinetic Model of the Liquid-phase Oxidation of Cyclohexane. I. Homogeneous Proceedings of the Process. *Kinetics and Catalysis*, 30: 954-958.

[43] Loncarevic, D., Krstic, J., Bankovic, P., Anic, S., Cupic, Z. (2007). Temperature Dependence of Catalytic Cyclohexane Partial Oxidation in A Polytetrafluoroethylene Reactor. *Russian Journal of Physical Chemistry A.*, 81: 1398-1401.

[44] Akhrem, A.A., Metelitsa, D.I., Skurko, M.E., (1975). Chemical Model of the Enzyme System for Hydroxylating Cyclohexane. *Bioorganic Chemistry*, 4: 307-316.

[45] Larsen, R.G., Saladino, A.C., Hunt, T.A., Mann, J.E., Xu, M., Grassian, V.H., Larsen, S.C. (2001). A Kinetic Study of the Thermal and Photochemical Partial Oxidation of Cyclohexane with Molecular Oxygen in Zeolite Y. *Journal of Catalysis*, 204: 440-449.

[46] Mahajani, S.M., Sharma, M.M., Sridhar, T. (1999). Uncatalyzed Oxidation of Cyclohexene. *Chemical Engineering Science*, 54: 3967-3976.

[47] Suresh, A.K., Sridhar, T., Potter, O.E. (1988). Autocatalytic Oxidation of Cyclohexane-Modeling Reaction Kinetics. *AlChE Journal*, 34: 69-80.

[48] Wang, J., Zhao, H., Zhang, X., Liu, R., Hu, Y. (2008). Oxidation of Cyclohexane Catalyzed by TS-1 in Ionic Liquid with Tert-butylhydroperoxide. *Chinese Journal of Chemical Engineering*, 16: 373-375.

[49] Selvam, P., Mohapatra, S.K. (2004). Synthesis, Characterization and Catalytic Properties of Mesoporous TiHMA Molecular Sieves: Selective Oxidation of Cycloalkanes. *Microporous and Mesoporous Materials*, 73: 137-149.

[50] Liu, X., He, J., Yang, L., Wang, Y., Zhang, S., Wang, W., Wang, J. (2010). Liquid-phase Oxidation of Cyclohexane to Cyclohexanone over Cobalt-Doped SBA-3. *Catalysis Communications*, 11: 710-714.

[51] Dapurkar, S.E., Sakthivel, A., Selvam, P. (2004). Mesoporous VMCM-41: Highly Efficient and Remarkable Catalyst for Selective Oxidation of Cyclohexane to Cyclohexanol. *Journal of Molecular Catalysis A: Chemical*, 223: 241-250.

[52] Wu, P., Bai, P., Loh, K.P., Zhao, X.S. (2010). Au Nanoparticles Dispersed on Functionalized Mesoporous Silica for Selective Oxidation of Cyclohexane. *Catalysis Today*, 158: 220-227.

[53] Aboelfetoh, E.F., Fechtelkord, M., Pietschnig, R. (2010). Structure and Catalytic Properties of MgO-supported Vanadium Oxide in the Selective Oxidation of Cyclohexane. *Journal of Molecular Catalysis A: Chemical*, 318: 51-59.

[54] Silva, F.P., Jacinto, M.J., Landers, R., Rossi, L.M. (2011). Selective Allylic Oxidation of Cyclohexene by a Magnetically Recoverable Cobalt Oxide Catalyst. *Catalysis Letters*, 141: 432-437